

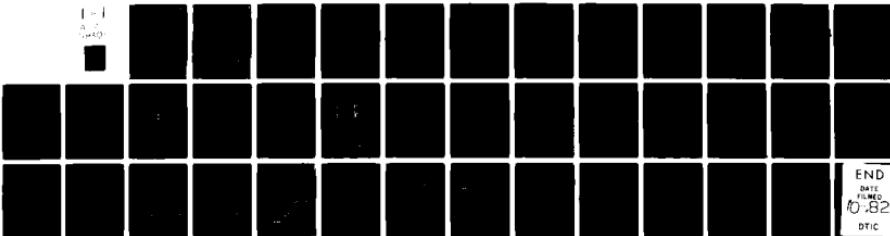
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FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF INORGANIC --ETC(U)
AUG 82 M S WRIGHTON N00014-75-C-0880

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"FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF
INORGANIC INTERFACES"

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Prepared for publication in the ACS Symposium Series
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Fuel and Electricity Generation from Illumination of Inorganic Interfaces

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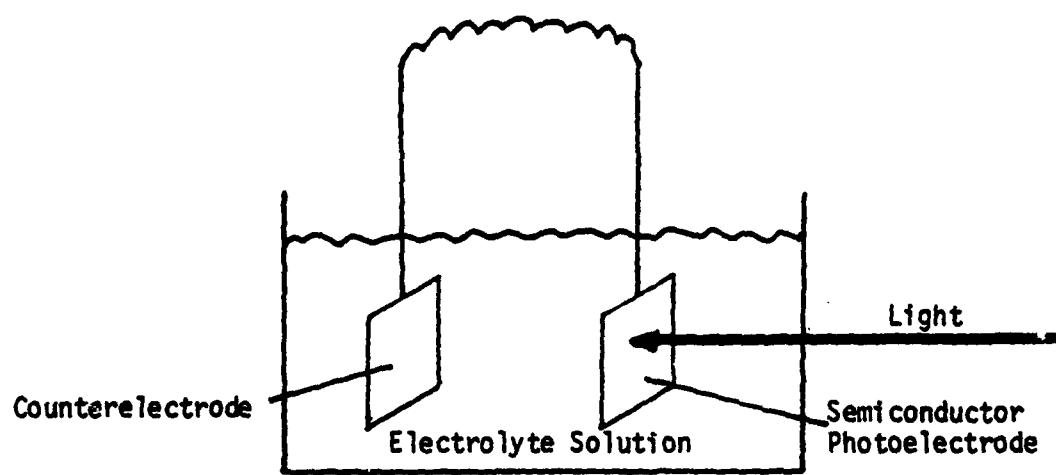
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Abstract: Semiconductor-based photoelectrochemical devices represent good systems for the sustained, direct conversion of light to chemical or electrical energy. The interfacial structure, energetics, and redox kinetics control the overall performance of such systems. Examples of improvements in efficiency and durability of photoelectrochemical cells stemming from chemical manipulations at semiconductor/liquid electrolyte interfaces illustrate the critical importance of understanding interface properties.

Introduction

Inorganic chemistry at interfaces is crucial to a large number of processes, systems, and devices that have practical consequence now and into the 21st century. Heterogeneous catalyst systems, batteries, fuel cells, field effect transistors, optical and acoustical recorders, sensors, solar cells, and even natural plant photosynthesis are all dependent on interfaces. It is becoming evident that characterization, synthesis, manipulation, and understanding of interfacial properties will comprise a significant fraction of the fundamental effort undergirding many practical applications of inorganic chemistry. With the advent of an arsenal of new spectroscopic probes it is apparent that chemically complex interfaces can be characterized with good resolution. The impact of the structural characterization of interfaces is likely to be as great as from the structural characterization that is commonplace for relatively small molecular entities. Elucidation of molecular structure plays a central role in the understanding of reactions and leads to insight into details of mechanism and electronic structure. Exploitation of interfaces in inorganic-based systems can continue with no new insights. However, as the 21st century approaches inorganic chemists have the opportunity to contribute heavily to the understanding of interfaces and rational application of basic knowledge to better use interfaces.

One current basic research endeavor involves the use of illuminated interfacial chemical systems to bring about the sustained conversion of optical energy to chemical or electrical energy. In fact, semiconductor-based photoelectrochemical cells like that in Scheme I represent the best chemical systems for the direct conversion of optical energy to electrical energy or to chemical energy in the form of high energy redox products.¹ In such devices the light-absorbing semiconductor electrode immersed in an electrolyte solution comprises a photosensitive interface where thermodynamically uphill redox processes can be driven with optical energy. Depending on the nature of the photoelectrode, either a reduction or an oxidation half-reaction can be light-driven with the counterelectrode being the site of the accompanying half-reaction. N-type semiconductors are photoanodes, p-type semiconductors are photocathodes,²⁻⁴ and intrinsic materials⁵ can be either a photoanode or a photocathode depending on the nature of the contact by both the liquid and the wire of the external circuit. Within the past decade remarkable progress has emerged from conscious efforts to understand and improve semiconductor-based photoelectrochemical cells. Systems based on n-type GaAs,^{6,7} n-type WSe₂,^{8,9}



Scheme I Semiconductor-based photoelectrochemical cell. Energy output may be in the form of electricity by putting a load in series in the external circuit or the output can be in the form of chemical energy as redox products formed at the electrodes. N-type semiconductors effect uphill oxidations upon illumination and p-type semiconductors effect uphill reductions under illumination. Either or both electrodes in the cell can be a photoelectrode.

and p-type InP^{10,11} have been shown to be able to convert sunlight with greater efficiency than the widely regarded minimum useful efficiency of 10% for large scale energy generation from sunlight in the United States.¹²

The aim of this presentation is to highlight both recent advances and to identify problems associated with illuminated semiconductor electrodes for optical energy conversion. Results from this laboratory will be highlighted. Practical applications, if they come at all, will be important in the 21st century and beyond. However, though the prospects for large scale energy generation from sunlight may appear dim, it is clear that existing fossil fuel reserves are finite, fission nuclear power has an uncertain future, and fusion does not work now and may not work in the future. Solar chemical conversion schemes do work on a large scale as evidenced by the natural photosynthetic apparatus. Existing solar insolation is far greater than man's needs. The research effort required to fully investigate interfacial solar conversion schemes is worth expending when viewed against the possible return and the prospect that other alternatives may prove unacceptable from a technical, social, political, economic, or safety standpoint.

Semiconductor/Liquid Electrolyte Interface Energetics

Schemes II and III represent the equilibrium interface energetics for ideal n- and p-type semiconductors, respectively, for contact by electrolyte solutions containing different redox reagents that vary in electrochemical potential, E_{redox} .^{2-4,13} For E_{redox} sufficiently negative for n-, or sufficiently positive for p-type, semiconductors the electrode behaves as a metallic electrode, not blocking the flow of electrons in either direction. This situation is analogous to the criteria for forming an ohmic contact to an n- or p-type semiconductor.¹⁴ When E_{redox} is between the top of the valence band, E_{VB} , and the bottom of the conduction band, E_{CB} , the p-type semiconductor is blocking to reductions and the n-type semiconductor is blocking to oxidations in the dark. The minority carrier (e^- or h^+ for p- or n-type semiconductors, respectively) is only available upon photoexcitation with $>E_g$ light and is driven to the interface, owing to the field in the semiconductor near the surface. The availability of the minority carrier at the interface upon photoexcitation allows oxidation with h^+ or reduction with e^- , and importantly the oxidizing power of the h^+ for n- and the reducing power for p-type semiconductors can be greater than that associated with the electrochemical potential (Fermi level), E_f , in the bulk of the semiconductor. This means that light can be used to drive thermodynamically non-spontaneous redox processes. The extent to which a process can be driven in an uphill sense is the photovoltage, E_V , that is given by equation (1) for ideal

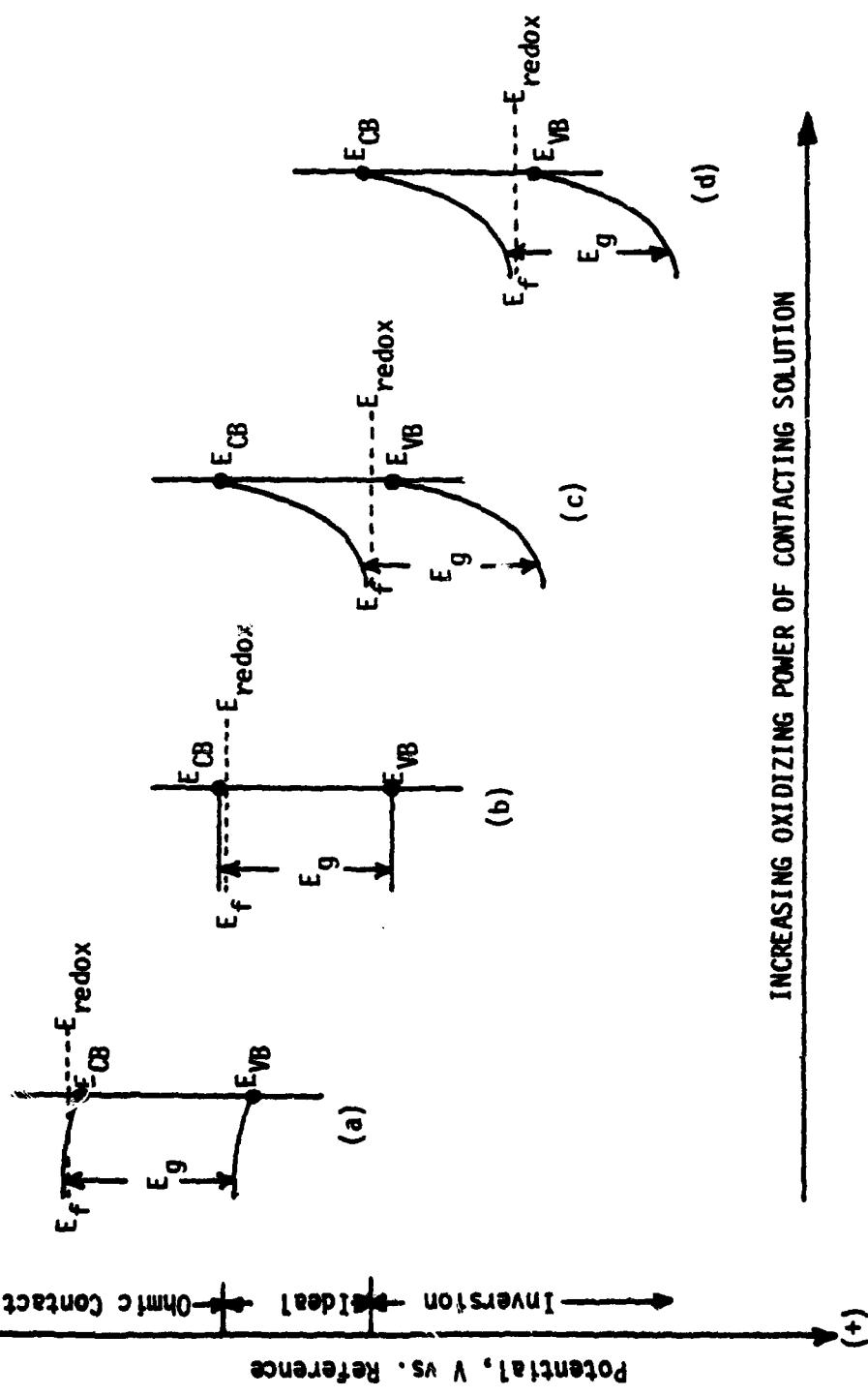
$$E_V = |E_{FB} - E_{redox}| \quad (1)$$

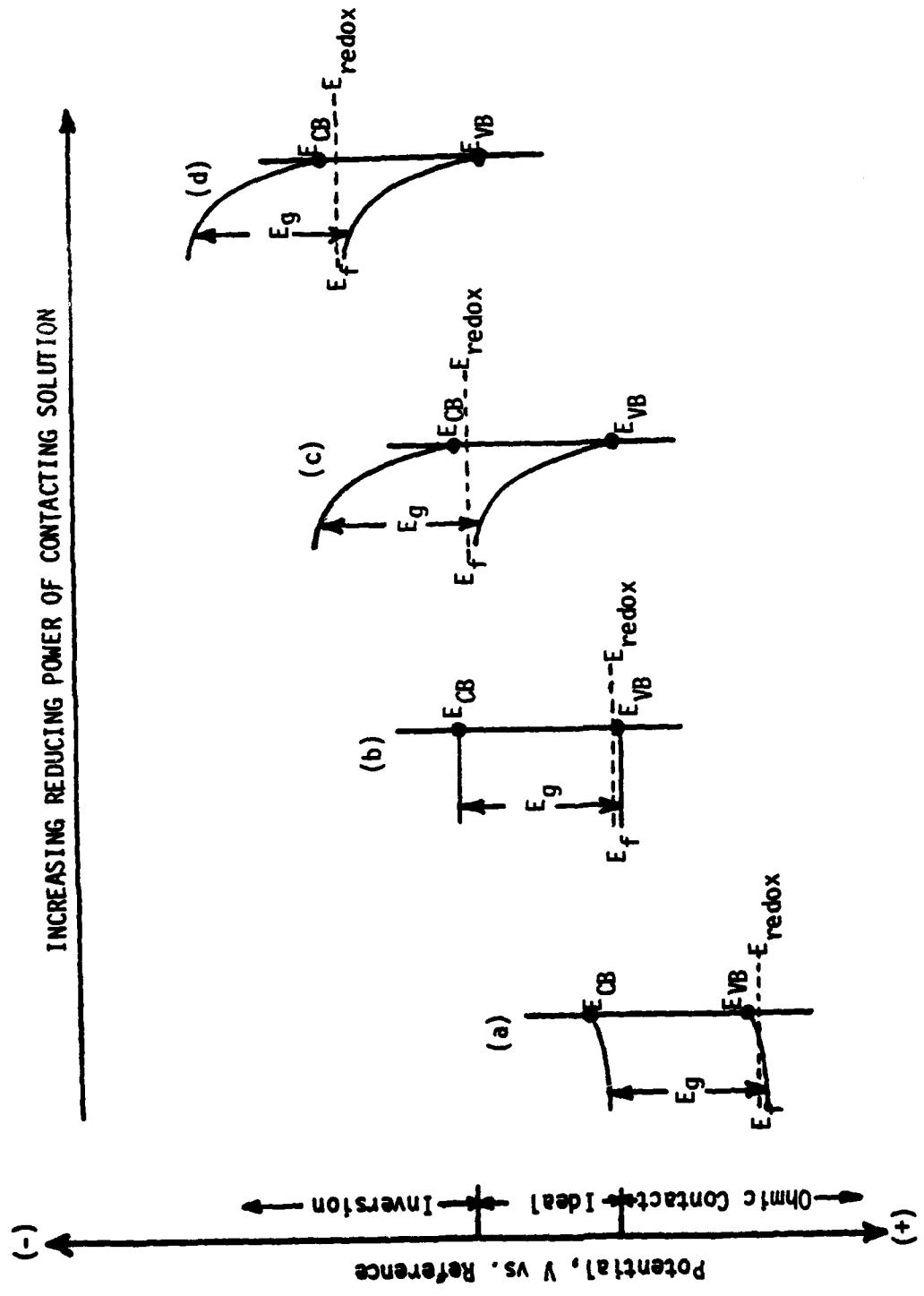
(For E_{redox} between E_{CB} and E_{VB})

semiconductors where E_{FB} is the flat-band potential, i.e. the value of E_f where the bands are not bent. For commonly used carrier concentrations E_{FB} is within 0.1 V of E_{VB} for p-type semiconductors, and for n-type semiconductors E_{FB} is within 0.1 V of E_{CB} . Thus, $>E_g$ illumination of a semiconductor electrode at open-circuit tends to drive E_f to E_{FB} , more positive for p-type

Scheme 11

Representation of the interface energetics for an ideal n-type semiconductor in contact with electrolyte solutions of differing E_{redox} . For E_{redox} more negative than the flat band potential, shown in (b), there is little band bending (no barrier) and the electrode is reversible with respect to the redox couple and is said to be in ohmic contact, (a). For E_{redox} between the flat band potential and some positive potential represented in (c) the drop in potential occurs across the semiconductor and the behavior is "ideal" in that the band bending varies according to eq. (1) of text. For more positive E_{redox} additional potential drop across the semiconductor does not occur, since the semiconductor is inverted at the surface, and the band edges effectively shift more positive as the potential drop occurs across the Helmholtz layer of the solution.





Scheme III

Representation of the interface energetics for an ideal p-type semiconductor in contact with electrolyte solutions of differing E_{redox}. The situation is analogous to the n-type semiconductor except that the more positive E_{redox} gives an ohmic contact and the most negative E_{redox} gives inversion. For E_{redox} between the flat band potential, (b), and some negative potential the behavior is "ideal" in that the band bending varies according to eq. (1) of the text.

electrodes and more negative for n-type electrodes compared to dark equilibrium where $E_f = E_{redox}$.

Ideally, the maximum value of E_y approaches the band gap, E_g , of the semiconductor. However, ~0.3 V of band bending is required to efficiently separate the $e^- - h^+$ pairs created by light. The separation of $e^- - h^+$ pairs is essential to obtain a high quantum yield for net electron flow, Φ_e . In any energy conversion application the efficiency, η , for the photoelectrode is given by equation (2), and since i is proportional to Φ_e it is desirable to

$$\eta = \frac{E_y \times i}{\text{Input Optical Power}} \quad (2)$$

i = photocurrent

obtain a large value of Φ_e . Good E_y at $i = 0$ (illuminated, open-circuit) or good i at $E_y = 0$ (illuminated, short-circuit) are both situations that give $\eta = 0$. The objective is to optimize the product of E_y and i in order to achieve the maximum efficiency. Figure 1 shows a steady-state photocurrent-voltage curve¹⁵ for an n-type WS_2 ($E_g = 1.4$ eV) photoanode-based cell for conversion of light to electricity employing the Br_2/Br^- redox couple and the inset shows the full cell energetics for operation at the maximum power point, the value of E_f when $E_y \times i$ is maximum. Figure 2 shows a similar curve for a cell based on p-type WS_2 employing $Fe(n^5-C_5Me_5)_2^{+/0}$ as the redox couple.¹⁶ In solar energy applications an E_g in the range 1.1-1.7 eV is desirable, since a single photoelectrode based device would have optimum solar efficiency, exceeding 20, for such band gaps.¹²

The WS_2 electrodes represent n- and p-type semiconductors that behave relatively ideally^{15,16} with respect to interface energetics in that the value of E_y does vary with E_{redox} according to equation (1) for E_{redox} within ~0.8 V of E_{FB} . However, for many electrode materials the variation in E_y does not follow equation (1).¹⁷ For example, n-type $CdTe$ ($E_g = 1.4$ eV) can give either a constant value of E_y (independent of E_{redox}) or a nearly ideal variation in E_y , Figure 3, depending on the pretreatment of the surface prior to use.¹⁸ The ability to improve the value of E_y from the constant value of ~0.5 V to ~0.9 V using a reducing surface pretreatment is clearly desirable, but at the same time certain oxidation reactions can be driven in an uphill sense using the oxidizing pretreatment that could not be done with the $CdTe$ pretreated with the reducing reagent.

For $CdTe$ it is evident that the surface pretreatment chemistry is related to the value of E_y . In fact, Auger and X-ray photoelectron spectroscopy reveal a correlation of the E_y vs. E_{redox} behavior related to the composition of the surface of $CdTe$.¹⁸ The oxidizing surface etch leaves a Te-rich overlayer that causes the $CdTe$ to behave as if it is coated with a metal having a work function that gives a Schottky barrier height of ~0.6 V. In the liquid junction system the analogue of Schottky barrier height is the $E_{redox} - E_{CB}$ or $E_{redox} - E_{VB}$ separation for p- or n-type semiconductors. If a Schottky barrier is immersed into a liquid electrolyte solution the value of E_y should be independent of E_{redox} , as found from n-type $CdTe$ after an oxidizing pretreatment.

Generally, when E_y is fixed for a wide range of E_{redox} the semiconductor is said to be "Fermi level pinned".¹⁷ Fermi level pinning simply means that the value of E_f at the surface of the semiconductor is pinned to some value relative to the band edge positions, independent of the electrochemical potential of a contacting solution or work function of a contacting metal. The pinning of the E_f is due to surface states of sufficient density and distribution. Thus, the presence of surface states can alter the behavior of a semiconductor photoelectrode with respect to output efficiency vs. E_{redox} owing to a limitation on E_y . The degree of alteration in behavior depends on the surface state distribution. For n-type CdTe the value of E_y is fixed to ~0.5 V, a relatively small fraction of the band gap. For p-type InP ($E_g = 1.3$ eV) it would appear that the surface state distribution is such that the value of E_y is fixed to ~0.8 V,¹¹ a much larger fraction of the band gap. Understanding and controlling surface states is thus crucial to development of efficient semiconductor-based devices.

Even for ideal (surface-state free) semiconductors the behavior with respect to E_y vs. E_{redox} can be confusing. For the ideal p- or n-type semiconductor sufficiently negative or positive E_{redox} , respectively, will result in carrier inversion at the surface of the semiconductor, Schemes II and III.^{14,19} In the region of E_{redox} where there is inversion the semiconductor photoelectrode can still effect uphill redox processes upon illumination and E_y can be independent of E_{redox} . The Fermi level, relative to the band edge positions, simply cannot be driven significantly more negative than E_{CB} or more positive than E_{VB} . Thus, for a range of E_{redox} the band edge positions vary with E_{redox} in a manner similar to when surface states between E_{CB} and E_{VB} pin the Fermi level. In the ideal case it is the high density of states from the valence or conduction band that eventually gives an E_y that is independent of E_{redox} .

When the observed value of E_y is a large fraction of E_g it is not easy to determine whether surface states pin E_f or whether a tailing density of valence or conduction band states effect pinning. Whenever the E_y exceeds $1/2E_g$ there is a measure of carrier inversion at the surface at dark equilibrium, but this does not mean that strong inversion is possible. Strong inversion can only occur when the region between E_{CB} and E_{VB} is sufficiently free of states that E_y can approach E_g . Generally, it is difficult to effect strong inversion when the semiconductor is in contact with any conductor, including liquid electrolyte solutions. The metal chalcogenides, MoS_2 , $MoSe_2$, WS_2 , and WSe_2 , seem to be closest to ideal of the semiconductors studied, though there still seems to be a role for surface states.^{15,16,20} A material such as n-type CdTe that gives a fixed E_y at $<1/2E_g$ must be one that is Fermi level pinned by states between E_{CB} and E_{VB} . Fermi level pinning would also appear to apply to photoelectrode materials such as $SrTiO_3$,²¹ TiO_2 ,²¹ InP,¹¹ GaAs,²² and Si.²³

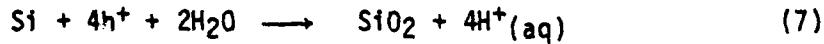
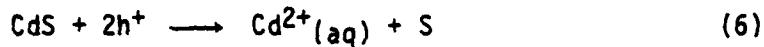
Manipulating surface states of semiconductors for energy conversion applications is one problem area common to electronic devices as well. The problem of Fermi level pinning by surface states with GaAs, for example, raises difficulties in the development of field effect transistors that depend on the ability to move the Fermi level at the surface. Interface electronic states need to be understood in all semiconductor-based devices and will continue to be the object of study for the foreseeable future.

The conclusions from these considerations are that semiconductor photoelectrodes can be used to effect either reductions (p-type semiconductors) or oxidations (n-type semiconductors) in an uphill fashion. The extent to which reaction can be driven uphill, E_y , is no greater than E_g , but may be lower than E_g owing to surface states between E_{CB} and E_{VB} or to an inappropriate value of E_{redox} . Both E_g and E_{redox} are properties that depend on the semiconductor bulk and surface properties. Interestingly, E_y can be independent of E_{redox} meaning that the choice of E_{redox} and the associated redox reagents can be made on the basis of factors other than theoretical efficiency, for a given semiconductor. Thus, the important reduction processes represented by the half-reactions (3)-(5) could, in principle, be effected with the same efficiency at a Fermi level pinned (or carrier inverted) p-type semiconductor photocathode. However, as is usual in chemical systems, thermodynamics relates what is possible, but kinetics rule whether a thermodynamically spontaneous process will occur at a practically useful rate.



Each of the reduction processes represented in (3)-(5) has great potential practical significance if it could be done efficiently using solar energy. However, each is a multi-electron process having poor heterogeneous kinetics at illuminated p-type semiconductors. Thus, the ability to exploit the available driving force from illumination of a semiconductor will depend on improvements in heterogeneous kinetics for these and other multi-electron redox processes. Success in this particular area will have practical consequence in the future even if semiconductor-based photoelectrochemical devices fail to prove useful. Development of better fuel cells depends on the improvement of heterogeneous redox kinetics of multi-electron processes. If fusion works and provides inexpensive electricity, chemical fuel formation via electrolytic processes may be useful. Again, heterogeneous kinetics must be improved. And clearly, heterogeneous catalytic chemistry will continue to be the key to efficient chemical production. The problem of poor heterogeneous kinetics for most fuel-forming reactions is thus one facet of a generic problem pervading much of chemistry.

One additional problem at semiconductor/liquid electrolyte interfaces is the redox decomposition of the semiconductor itself.²⁴ Upon illumination to create $e^- - h^+$ pairs, for example, all n-type semiconductor photoanodes are thermodynamically unstable with respect to anodic decomposition when immersed in the liquid electrolyte. This means that the oxidizing power of the photogenerated oxidizing equivalents (h^+ 's) is sufficiently great that the semiconductor can be destroyed. This thermodynamic instability is obviously a practical concern for photoanodes, since the kinetics for the anodic decomposition are often quite good. Indeed, no non-oxide n-type semiconductor has been demonstrated to be capable of evolving O_2 from H_2O (without surface modification), the anodic decomposition always dominates as in equations (6) and (7) for n-type CdS ²⁵ and Si ,²⁶ respectively. Protecting visible light



responsive n-type semiconductors from photoanodic decomposition has been a major activity in the past half dozen years and will continue to be an issue of concern. The p-type semiconductors have not been plagued by gross durability problems, but thermodynamic instability can be a problem in some cases.^{24,27} Interestingly, the redox decomposition processes of semiconductors are multi-electron processes that can be sufficiently slow that kinetic competition with desired redox processes can be successful to bring about sustained generation of energy-rich products or electricity from photoexcitation of a photoanode.

Suppression of Photocorrosion of Photoanodes and Manipulation of Kinetics for

Anodic Processes

In 1976 the first sustained conversion of visible light to electricity using an n-type semiconductor-based cell (CdS ($E_g = 2.4$ eV) or CdSe ($E_g = 1.7$ eV)) was reported.^{25,27} In the ensuing six years remarkable progress has been realized in this area. The key has been to find reducing reagents, A, that can capture photogenerated oxidizing equivalents, h^+ , at a rate that precludes decomposition of the semiconductor, equation (8). The reverse process, equation (9), can then be effected at the counterelectrode to complete



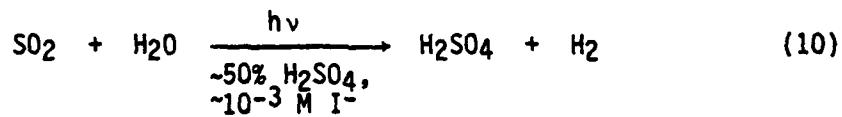
a chemical cycle involving no net chemical change, but yield significant efficiency for electricity generation. Now, a variety of n-type semiconductor/solvent/electrolyte/ A^+ /A/counterelectrode systems are known to comprise efficient, durable visible light energy to electrical energy.^{6-9,15,25,27,28}

Often, there is a potential regime where the process represented by (8) is completely dominant compared to the anodic decomposition of the semiconductor. In some cases, e.g. $\text{CdS}/\text{Sn}^{2-}$,²⁹ $\text{CdTe}/\text{Te}^{2-}$,²⁹ and $\text{MoSe}_2/\text{I}_3^-$,³⁰ the redox species interact strongly with the electrode material resulting in changes in E_{FB} . Such strong interactions can be useful in protecting the semiconductor. In the examples cited above, E_{FB} shifts more negative reducing the tendency for anodic decomposition and opening a wider potential regime where the desired oxidation process can be effected without completion from anodic decomposition.

The unique interactions of a semiconductor with solution species, such as MoSe_2 with I_3^- ,³⁰ are very likely the sorts of situations that will lead to the first applications of semiconductor photoelectrochemical devices for photochemical synthesis of redox products. Generally, the practical competition will come from conventional, including electrochemical, methods for producing redox reagents. When the semiconductor electrode has unique surface chemistry

this can change the product distribution and in some cases it may be that the semiconductor may be the only surface at which a desired reaction will occur efficiently. However, even when a semiconductor is the electrode material of choice it is not clear that light would be used. The desirable interactions that exist for a p-type photocathode, for example, would likely exist as well for the oppositely doped, n-type, material. The reductions that require light at the p-type electrode can be effected in the dark at the n-type material. Also, degenerately doped semiconductors often behave well in the dark and are not blocking to any redox processes. However, the unique chemistry of semiconductor surfaces needs to be elucidated before a verdict can be reached regarding the practical consequences.

The strong interaction of the I_3^-/I^- redox system with the metal dichalcogenide materials was recently exploited³¹ to bring about the visible light-driven process represented by equation (10). In 50% by weight H_2SO_4 the reaction as written requires ~0.3 V or driving force, a good match to the

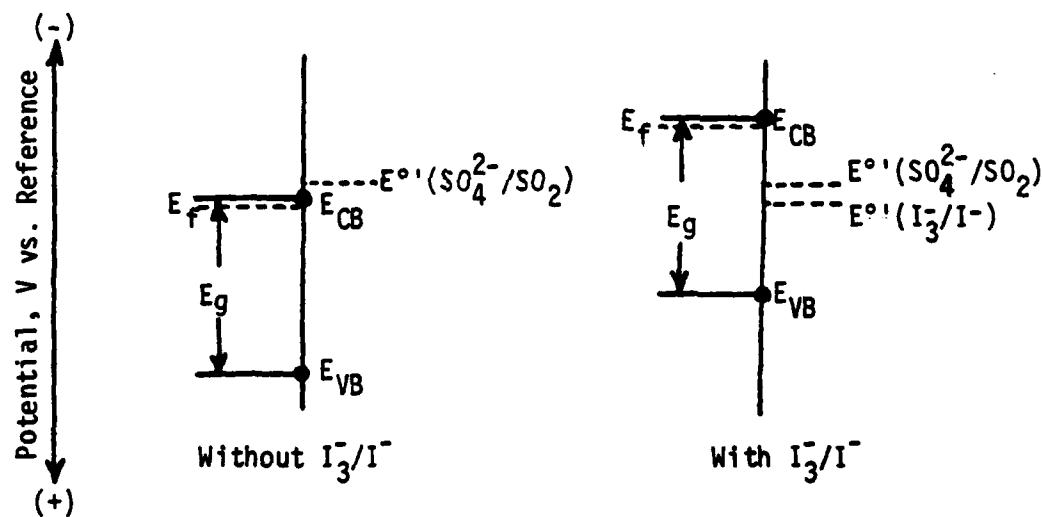
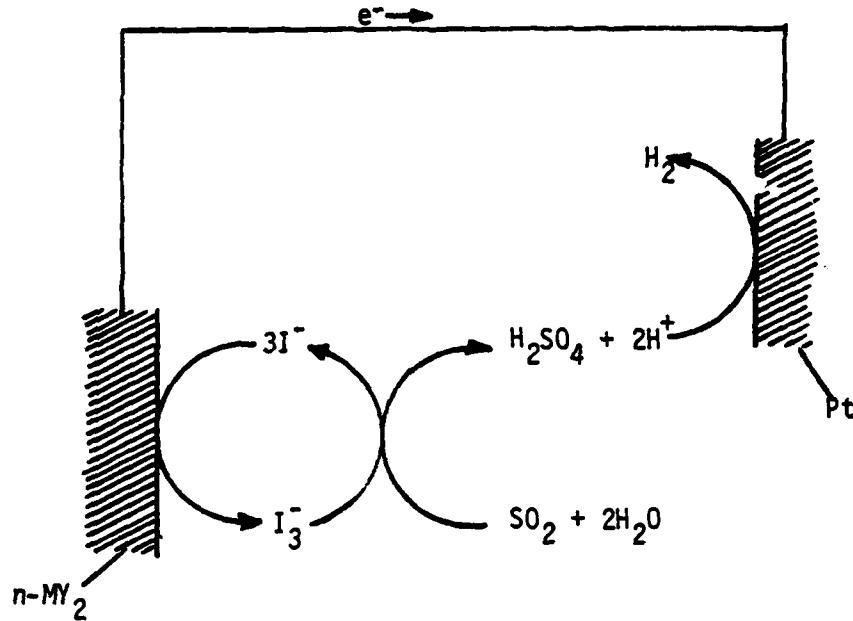


photovoltage at the maximum power point for n-type WS_2 -based cells for the oxidation of I^- .¹⁵ But the oxidation of SO_2 to SO_4^{2-} in H_2SO_4 has poor kinetics³² and does not compete with photoanodic decomposition of the electrode. Further, $E_{redox}(SO_4^{2-}/SO_2)$ is such that equation (1) predicts a very small photovoltage.³² The I_3^-/I^- , though, interacts to shift E_{FB} of WS_2 favorably to give a good E_V with respect to $E_{redox}(SO_4^{2-}/SO_2)$ and simultaneously provides a mechanism for the oxidation of SO_2 , since the I_3^- rapidly oxidizes SO_2 to SO_4^{2-} , Scheme IV. Thus, the I_3^-/I^- serves as a redox mediator and favorably alters the interface energetics to give a good E_V and a potential window of durability. The visible light-driven reaction represented by equation (10) is one of the most efficient optical to chemical energy conversions (up to ~14% from 632.8 nm light) known. The system illustrates the complex relationships that must be understood in order to efficiently drive multi-electron redox processes.

The suppression of photoanodic corrosion is not always difficult. For example, metal dichalcogenides are not durable in aqueous 0.1 M KCl ; equation (11) represents the photoanodic decomposition process for MoS_2 .³³ However, the



oxidation of low concentrations of Cl^- occurs in CH_3CN solution with 100% current efficiency.³⁴ Even in aqueous solution the oxidation of Cl^- can be effected at sufficiently high Cl^- activity.^{15,35} In aqueous 15 M $LiCl$ the oxidation of Cl^- has 100% current efficiency. The high $LiCl$ concentration yields very high Cl^- activity and lower activity of H_2O , both contributing to the improved durability of illuminated n-type MoS_2 .³⁵ Thus, these experiments show, not surprisingly,²⁴ that the medium in contact with the semiconductor can alter the overall interfacial chemistry, even though Cl^- is available as a reductant in each case. The ability to effect the sustained generation of Cl_2 at an illuminated interface shows that potent oxidants can be made

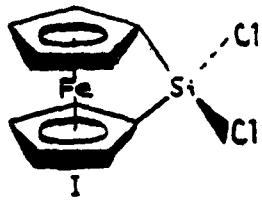


Scheme IV Representation of the I_3^-/I^- mediated oxidation of SO_2 at illuminated metal dichalcogenide photoanodes (top) and interface energetics without and with I_3^-/I^- in $6M H_2SO_4/1M SO_2$ for MoS_2 after ref. 31. Note that in the absence of the mediator system the photovoltage for the SO_2 oxidation would be expected to be negligible. The adsorption of the I_3^-/I^- is unaffected by the SO_2 so the negative shift of the flat band potential can be exploited to give a photovoltage for the desired process with the I_3^-/I^- system simultaneously providing an acceleration of the SO_2 oxidation.

photochemically; Cl_2 is thermodynamically more potent, and kinetically more aggressive, than O_2 .

The ability to manipulate the anodic corrosion problem using high concentrations of redox active electrolyte also makes possible the sustained oxidation of Br^- at illuminated metal dichalcogenide-based cells, Figure 1.¹⁵ The use of high concentrations of electrolyte has proven valuable in situations involving other photoanode materials, notably n-type Si.^{36,37}

Reducing photoanodic corrosion with high concentrations of redox active materials led to the conclusion that redox reagents covalently anchored to the photoelectrode might prove useful.³⁸ For example, research showed that n-type Si could be a durable photoanode in $\text{EtOH}/0.1 \text{ M} [\text{n-Bu}_4\text{N}] \text{ClO}_4/\text{Fe}(\pi^5\text{-C}_5\text{H}_5)_2^{+}/0$ for the generation of electricity.²⁶ The $\text{Fe}(\pi^5\text{-C}_5\text{H}_5)_2$ is a fast, one-electron reductant that is durable and gives a durable oxidation product. Subsequent study showed that the reagent represented by I can be polymerized and

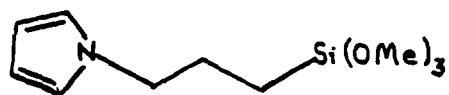


attached to the surface of n-type Si to protect it from photoanodic corrosion.³⁸⁻⁴⁰ The important result is that once the electrode is made durable using the surface-confined redox system, $[\text{A}^+/\text{A}]_{\text{surf.}}$, then the photo-electrode can be used to sustain many oxidation processes, say $\text{B} + \text{B}^+$, where B itself is not successful in competing with the anodic corrosion of the electrode. The ability to photooxidize B would then depend on the thermodynamics and kinetics for the interfacial process represented by equation (12) and not the kinetics for h^+ capture by B. It has been shown that



n-type Si derivatized with I is capable of effecting the photoassisted oxidation of a variety of reagents in H_2O solvent, where the decomposition (7) is most severe.⁴⁰ In several cases it has been established that the process represented by (12) represents the dominant path for production of B^+ . Thus, in principle, the molecular properties of the surface-confined reagent could be exploited to effect specific reactions. For the surface species derived from I the oxidizing power is fixed to $\sim 0.45 \text{ V vs. SCE}$, the formal potential, E° , of the surface reagent.⁴¹ However, the $\text{Fe}(\pi^5\text{-C}_5\text{H}_5)_2^{+}/0$ systems are outer-sphere reagents and do not offer any basis for selectivity other than the potential. However, such species may prove useful in facilitating the redox reactions of biological reagents, vide infra.

Several groups have recently shown^{36,42-44} that photoanode materials can be protected from photoanodic corrosion by an anodically formed film of "polypyrrole".⁴⁵ The work has been extended⁴⁶ to photoanode surfaces first treated with reagent II that covalently anchors initiation sites for the



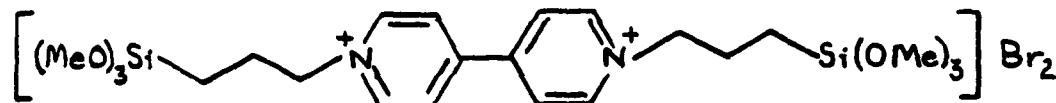
II

formation of polypyrrole. The result is a more adherent polypyrrole film that better protects n-type Si from photocorrosion. Unlike the material derived from polymerization of I, the anodically formed polypyrrole is an electronic conductor.⁴⁵ This may prove ultimately important in that the rate of ion transport of redox polymers may prove to be too slow to be useful in attaining useful photocurrent densities. For the electronically conducting polymer the rate would not be limited by ion transport.

At this point it is evident that there are many approaches to the sustained conversion of visible light using photoanodes. The approaches based on strong interaction, e.g. $WS_2/I_3^-/I^-$,¹⁵ or modified surfaces, e.g. derivatized n-type Si,³⁸⁻⁴⁰ seem most interesting since the unique properties of the interface can be exploited at the molecular level. Significantly, the generation of potent oxidants such as Br_2 or Cl_2 can be effected using visible light and with reasonably good efficiency but without electrode deterioration.

Improving the Kinetics for Hydrogen Generation from P-Type Semiconductors

No naked semiconductor photocathode has been demonstrated to have good kinetics for the evolution of H_2 , despite the fact that the position of E_{CB} in many cases has been demonstrated to be more negative than $E^\circ(H_2O/H_2)$. This means that electrons excited to the conduction band have the reducing power to effect H_2 evolution, but the kinetics are too poor to compete with $e^- - h^+$ recombination. The demonstration that N,N'-dimethyl-4,4'-bipyridinium, MV^{2+} , could be efficiently photoreduced at illuminated p-type Si to form MV^+ in aqueous solution under conditions where $E^\circ(MV^{2+/+}) = E^\circ(H_2O/H_2)$ when no H_2 evolution occurs establishes directly that the thermodynamics are good, but the kinetics are poor, for H_2 evolution.^{23,47} The ability to efficiently reduce MV^{2+} to MV^+ at illuminated p-type Si led to studies of the surface derivatizing reagent III for use as an electron acceptor on photocathode surfaces.⁴⁸

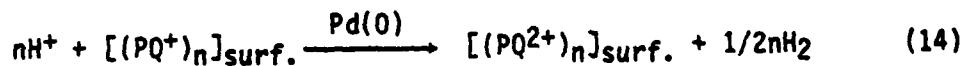
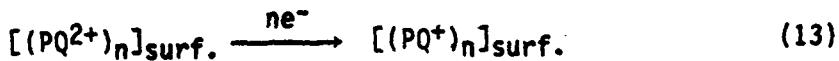


III

Subsequent deposition of Pd(0) by electrochemical reduction of low concentrations of aqueous $PdCl_4^{2-}$ leads to the interface represented in Scheme V.⁴⁹ The Pd(0) is crucial to bring about equilibration of the surface-confined viologen reagent, $[(PQ^{2+/+})_n]_{surf.}$, with the H_2O/H_2 couple. The $[(PQ^{2+/+})_n]_{surf.}/Pd(0)$ catalyst system can, in principle, be used on any photocathode surface to improve H_2 evolution kinetics.

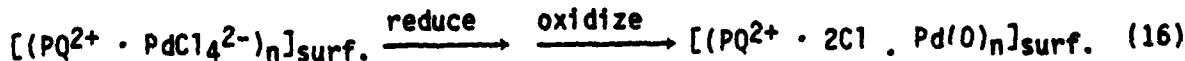
The improvement in photoelectrochemical H₂ evolution efficiency using the $[(PQ^{2+}/+)_n]_{surf.}/Pd(0)$ system is reflected by the data in Figure 4. For the naked surface, H₂ evolution barely onsets at $E^\circ(H_2O/H_2)$. For the photoelectrode bearing $[(PQ^{2+}/+)_n]_{surf.}/Pd(0)$ the onset for H₂ evolution is up to ~500 mV more positive than $E^\circ(H_2O/H_2)$. The extent to which the onset is more positive than $E^\circ(H_2O/H_2)$ is E_V . It is obvious that the modified photoelectrode gives superior performance.

The mechanism of the catalysis for the p-Si/ $[(PQ^{2+}/+)_n]_{surf.}/Pd(0)$ system is represented by equations (13) and (14). The $E^\circ[(PQ^{2+}/+)_n]_{surf.} = -0.55 \pm 0.5$ V vs. SCE,⁵⁰ independent of pH, whereas $E^\circ(H_2O/H_2)$ varies with pH.



Thus, the catalyzed process represented by (14) is only downhill for sufficiently low pH; at the lower pH's the driving force is greater and the rate is faster. However, as the pH is lowered E_V becomes smaller. This leads to an optimum in overall energy conversion efficiency at pH = 4. For monochromatic 632.8 nm light the efficiency for photoassisted H₂ evolution is up to ~5% whereas naked electrodes have negligible efficiency.^{49,50}

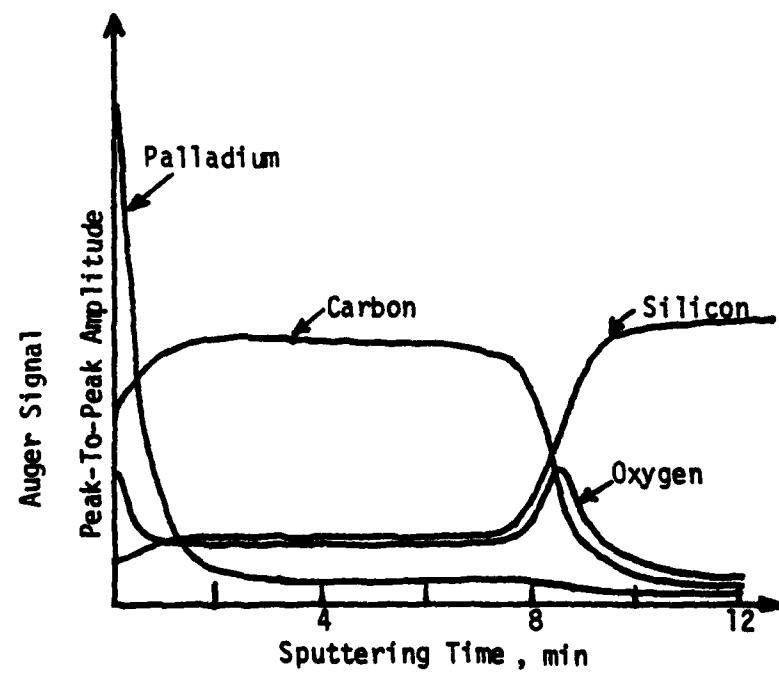
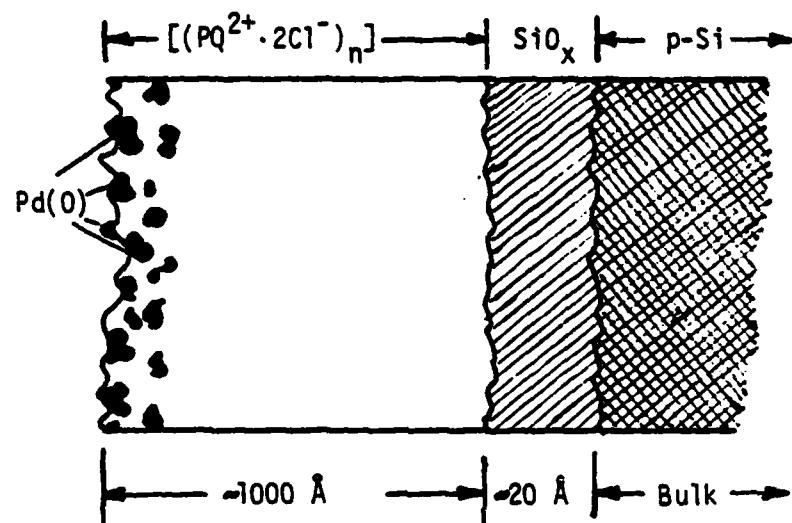
The $[(PQ^{2+}/+)_n]_{surf.}$ system can also be employed with Pt(0)⁵⁰ as the catalyst instead of Pd(0). Both Pt(0) and Pd(0) have excellent H₂ evolution kinetics. One virtue of Pd(0) is that it is much more easily detected by Auger electron spectroscopy than is Pt(0).⁴⁹ Auger electron spectra taken while sputtering the surface with Ar⁺ ions have led to the establishment of interface structures like that represented in Scheme V. Typically, 10⁻⁸ mol/cm² of PQ²⁺ centers and ~10⁻⁸ mol/cm² of Pd(0) are used to give an overlayer of ~2000 Å in dimension. A key feature of the interface represented by Scheme V is that there is no Pd(0) at the p-type Si/SiO_x surface. This means that the only mechanism for equilibrating H₂O/H₂ with the photogenerated reducing equivalents is via the $[(PQ^{2+}/+)_n]_{surf.}$ system. Studies have also been done with Pt(0) or Pd(0) dispersed throughout the polymer from III via the sequence represented by equations (15) and (16) for Pd(0).⁴⁹ In such cases there is at least a small



amount of Pd(0) at the p-type Si/SiO_x surface. The Pd(0) at the p-type Si/SiO_x surface should be responsible for some H₂ evolution current density, since the direct deposition of Pd(0) or Pt(0) (without III) onto p-type Si/SiO_x does improve H₂ evolution dramatically.^{50,51} Indeed, the direct deposition of catalytic metals onto p-type InP has led to a demonstration of ~12% efficiency for the solar-assisted production of H₂.⁵²

The ability to efficiently catalyze the H₂ evolution with a metal deposited onto the p-type semiconductor raises the legitimate question of why

Scheme V Representation of the catalytic p-type Si photocathode for H₂ evolution prepared by derivatizing the surface first with the reagent III in the text followed by deposition of approximately an equimolar amount of Pd(0) by electrochemical deposition. The Auger/depth profile analysis for Pd, Si, C, and O is typical of such interfaces, ref. 49, for coverages of approximately 10⁻⁸ mol of PQ²⁺ per cm².



use III at all, let alone attempt to prepare and exploit the more ordered interface represented by Scheme V. In theory, the efficiency of all devices based on a given semiconductor would be the same. The direct deposition of Pt(0) or the use of $[(PQ_2^{2+})_n]_{\text{surf.}}/Pd(0)$ are both ways of catalyzing the H₂ evolution. A problem with the redox polymers, as already mentioned, is that rate is likely to be ion transport limited. A problem with Pt(0) and Pd(0) is that they often give an ohmic contact, rather than a Schottky barrier, with p-type semiconductors. For example, in attempting to catalyze H₂ evolution from illuminated p-type WS₂ by electrochemically depositing Pt(0) or Pd(0) a large percentage of the electrodes give an ohmic contact.¹⁶ This results in no photoeffects from the electrode. A uniform coating with the redox polymer from III gives a reproducible, photosensitive surface that can be used to generate H₂ via Pd(0) or Pt(0) deposited on the outermost surface. Neither of the approaches has led to sufficiently durable catalysts that practical devices are at hand; the Pt(0) or Pd(0) is very easily poisoned. Surprisingly, the $[(PQ_2^{2+})_n]_{\text{surf.}}$ polymer does not suffer deterioration on the timescale of loss of activity of the Pd(0) or Pt(0) catalyst.

The synthesis of catalytic photocathodes for H₂ evolution provides evidence that deliberate surface modification can significantly improve the overall efficiency. However, the synthesis of rugged, very active catalytic surfaces remains a challenge. The results so far establish that it is possible, by rational means, to synthesize a desired photosensitive interface and to prove the gross structure. Continued improvements in photoelectrochemical H₂ evolution efficiently can be expected, while new surface catalysts are needed for N₂ and CO₂ reduction processes.

A Role for Biological Redox Catalysts?

The enzymes hydrogenase, nitrogenase, and formate dehydrogenase can be used to equilibrate reducing reagents with H₂O/H₂, N₂NH₃, and CO₂/HCOOH, respectively.⁵³ In no case do the enzymes involve expensive noble metals as catalysts. Practical considerations aside, the multi-electron transfer catalysis effected by enzymes provides an existence proof for desired photoelectrode catalysts. One of the major difficulties is that large biological redox reagents are often unresponsive at electrode surfaces. For a variety of reasons the heterogeneous electron transfer kinetics for large biological reagents are poor. However, small redox reagents dissolved in solution do equilibrate rapidly with the large biological reagents.⁵⁴ Interestingly, MV⁺, for example, will effect reduction of H₂O, N₂, or CO₂ when the proper enzyme is present as a catalyst.⁵³ The use of surface-confined, fast, one-electron, outer-sphere redox reagents like those derived from I or III as redox mediators for biological reagents would seem to represent an excellent approach to the equilibration of the electrode with the biological reagents.

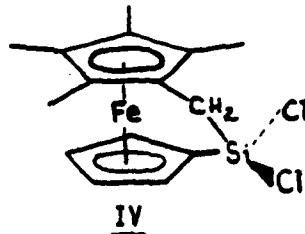
Experiments relating to the oxidation and reduction of ferro- and ferricytochrome c, cyt c(red) and cyt c(ox) from horse heart, establish that photoelectrodes derivatized with molecular reagents can give significantly improved response to biological redox reagents.^{55,56} The cyt c provides an example of a readily accessible biomolecule that generally has poor kinetics at

electrode surfaces.⁵⁷ The first experiments concerned electrodes derivatized with III.⁵⁵ The fact that MV^+ rapidly reduces cyt c(ox) to cyt c(red) led to the use of the $[(PQ^{2+}/^+)_n]_{surf.}$ for this purpose.⁵⁸ The E°' (cyt c(ox))/cyt c(red)) is ~ 0.02 V vs. SCE⁵⁵ and the reaction represented by equation (17) is

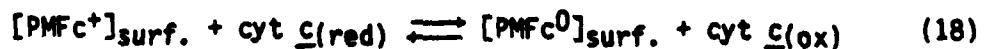


thus downhill by ~ 0.5 V. Interestingly, the process represented by (17) was shown to account for the reduction of cyt c at illuminated p-type Si functionalized with III.⁵⁵ The reduction of cyt c(ox) at electrodes derivatized with III is mass transport limited and independent of coverage of PQ^{2+} centers on the electrode from $\sim 10^{-10}$ to 10^{-8} mol/cm². Naked electrodes do not respond to the cyt c(ox) in the same potential range. Inasmuch as adsorption of cyt c, or impurities contained in it, onto most electrodes leads to overall poor kinetics, it is particularly noteworthy that high concentrations of cyt c(ox) can be reduced with good kinetics via the $[(PQ^+)_n]_{surf.}$. Thus, the modification of electrode surfaces with III brings about improvement in response with respect to reduction of cyt c(ox).

While experiments with the cyt c(ox) at $[(PQ^{2+}/^+)_n]_{surf.}$ do establish a point, the disparity E°' of the reagent and the mediator precludes the claims that electrodes can in fact equilibrate with the biological reagent. The synthesis of IV has led to the demonstration that derivatized electrodes can be



equilibrated with biological redox reagents.⁵⁶ Representing the surface species from IV by $[PMFc^{+}/^0]_{surf.}$, the $E^\circ' [PMFc^{+}/^0]_{surf.} = +0.04$ V vs. SCE, that is very close to the E°' for cyt c. Conventional Pt electrodes derivatized with IV can be used to oxidize cyt c(red), or reduce cyt c(ox) near the E°' of cyt c, via the equilibrium process represented by equation (18).



Importantly, n-type Si electrodes derivatized with IV can be used in aqueous electrolyte solution at pH = 7 and the process represented by equation (19) can



be effected in an uphill sense, $E_V \sim 300$ mV. As on the Pt surface, the $[PMFc^+]_{surf.}$ on n-type Si is capable of effecting the oxidation of cyt c(red). Thus, the n-type Si/ $[PMFc^{+}/^0]_{surf.}$ electrode can be used to effect the uphill oxidation of cyt c(red). The rate constant for reaction represented by equation (20) is $> 10^3$ M⁻¹s⁻¹. The observed heterogeneous electron rate constant is $> 1 \times 10^{-4}$ cm/s for a variety of electrodes independently prepared,



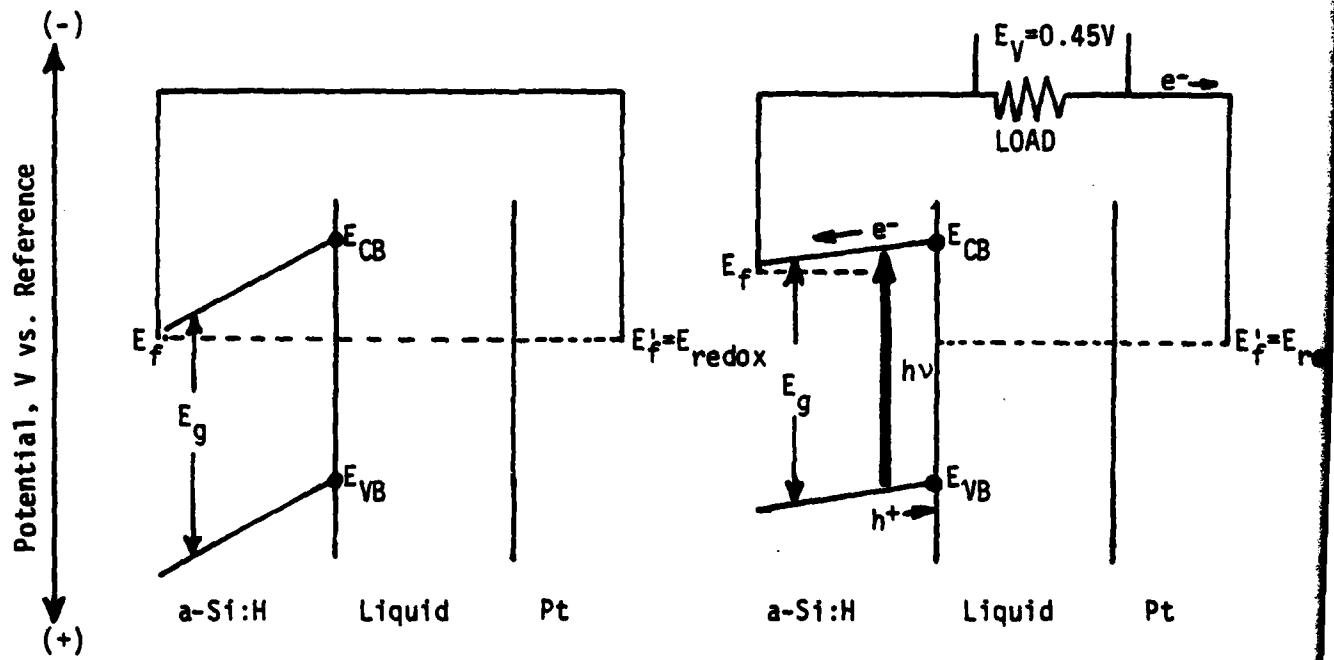
representing substantial improvement compared to naked electrodes that give negligible rates under the same conditions.⁵⁶ Significantly, as for $[(\text{PQ}_2^{\text{2-}}/\text{+})_n]_{\text{surf.}}$, the $[\text{PMFc}^0]_{\text{surf.}}$ is useful at high concentrations of cyt c. Very pure, low concentration cyt c apparently responds well at conventional electrodes, but small amounts of decomposition or impurities cause severe problems from adsorption.⁶⁰ The surface reagents from III or IV apparently minimize the adsorption problems, while providing a mechanism for exchanging electrons with the electrode.^{55,56} Preliminary results have established that hydrogenase can equilibrate with the polymer derived from III, suggesting that the one-electron polymers from III and IV can in fact come into redox equilibrium with multi-electron transfer catalysts for reactions of possible importance in energy conversion.

Large Area Photosensitive Materials

The studies described so far have concerned relatively small, ~0.1-1 cm², single-crystal photoelectrode materials. Promising results have been obtained in that there are a variety of durable, efficient paths to generation of high energy chemicals or electricity. However, single-crystal photoelectrode materials are likely to remain too expensive for significant practical development. The question is whether the basic results from single-crystal systems can be applied to large area photosensitive materials not necessarily fabricated from single crystals. In this area as well some promising results have been obtained. Thin film and/or polycrystalline GaAs⁶¹ and CdX⁶² photoanodes have been shown to have relatively good efficiency compared to their single-crystal analogues.

Recently, results from amorphous hydrogenated silicon, a-Si:H, $E_g = 1.7$ eV, obtained in a glow discharge of SiH₄ show significant promise. Solid state devices from solar to electrical energy conversion based on absorption of light by a-Si:H have been shown to have almost 10% efficiency⁶³ and it is believed that a-Si:H can be produced inexpensively and uniformly in large areas.

In principle, intrinsic photoconductors such as a-Si:H can be good photoelectrodes.^{5,64} Scheme VI shows the approximate interface situation for a recently reported a-Si:H-based cell for the generation of electricity.⁶⁴ Critically, the intrinsic thin film (1-4 μ) of a-Si:H was deposited onto a very thin (~200 Å) heavily n-doped a-Si:H layer on stainless steel in order to assure that the Fermi level contacts the bottom of the conduction band. This means that E_{redox} positions of E_{CB} will result in a field across the photoconductor such that photogenerated h^+ 's will be driven toward the electrolyte/redox couple solution. For E_{redox} close to E_{g} the E_V would be expected to approach E_g as for an n-type semiconductor photoanode. As for any other photoanode the a-Si:H is susceptible to photoanodic decomposition, but the corrosion can be completely suppressed by using the 0.1 M $[\text{n-Bu}_4\text{N}]^+ \text{ClO}_4^-$ / EtOH / $\text{Fe}(\text{n}-\text{C}_5\text{H}_5)_2^{+/\text{0}}$ electrolyte/redox couple solution, Figure 5. Interestingly, the sustained conversion of 632.8 nm light is just as efficient for the intrinsic a-Si:H photoanode as for single-crystal n-type Si electrodes under the same conditions.⁵



Scheme VI Representation for the interface energetics for intrinsic a-Si:H at short-circuit, dark equilibrium with ferricenium/ferrocene in EtOH/electrolyte solution (left) and under illumination with 632.8 nm light with a load in series in the external circuit (right). The diagrams are adapted from data in ref. 65 for intrinsic a-Si:H (1-4 μ thick) on stainless steel first coated with heavily n-doped a-Si:H (200 \AA thick) to insure an ohmic contact near the bottom of the conduction band. In typical experiments E_{redox} is +0.4 V vs. SCE.

The surface of a-Si:H can also be derivatized with reagent I and the E_{y} is ~ 750 mV compared to $E_{\text{y}} = 500$ mV on single crystal n-type Si.⁵ This result suggests that a-Si:H could be durable in aqueous solutions via protection by the surface reagent. As for n-type Si this would allow the use of large area, efficient a-Si:H to effect a variety of light-driven oxidation processes.

Summary

Semiconductor-based photoelectrochemical cells can effect the sustained, direct conversion of light to chemical or electrical energy with good efficiency. There are several approaches to suppressing the photocorrosion of n-type semiconductor photoanodic materials, all depending on the manipulation of interface properties such as structure, energetics, and kinetics. The visible light-driven generation of Cl_2 from photoanodes represents the most potent oxidant generated from non-oxide electrodes. Output parameters depend on surface properties as reflected in experiments with reducing vs. oxidizing pretreatments for n-type CdTe. Interfacial redox kinetics can be modified by rational means as illustrated with results for photocathodes modified to improve H_2 evolution kinetics. However, much more work remains to be done on multi-electron processes to bring about improvements in kinetics. Certain enzymes may prove useful in N_2 , CO_2 , or H_2O reduction. Progress in relatively efficient, large area, inexpensive photoelectrode materials has been made, with a-Si:H being one example. At this point the performance of interfacial inorganic chemistry systems for energy conversion is sufficiently good that they cannot be ruled out as contenders for large scale energy generation. The near-term, pre-2000 charter is to fully elaborate the basic science underlying the interfacial systems with a conscious effort directed toward efficient (>10%) durable, and inexpensive systems for the direct production of energy-rich redox products from abundant, inexpensive resources such as H_2O and CO_2 . It is too early to focus on fuel vs. electricity generation as the ultimate objective. Many of the requirements for both outputs are the same but fuel generation poses the greatest challenge, since useful fuel generation will require new multi-electron transfer catalysts.

Acknowledgements

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Figure Captions

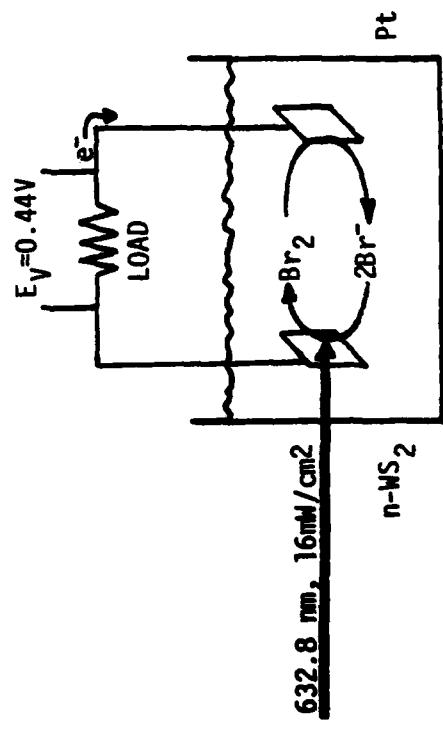
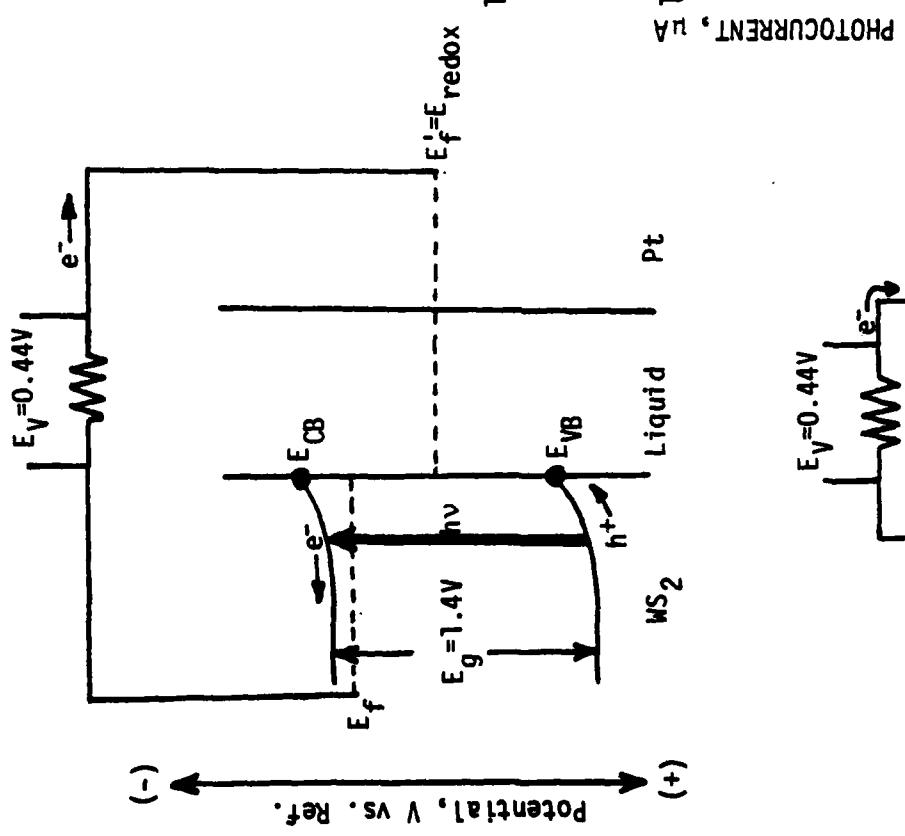
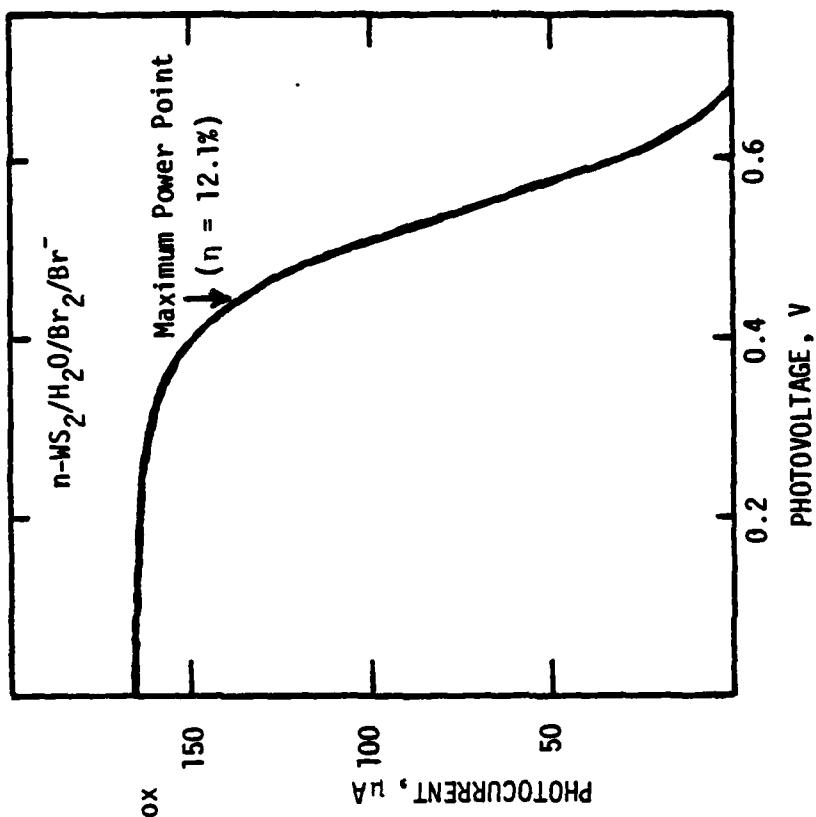
Figure 1. Cell (lower left), cell energetics at maximum power point (upper left) and output characteristics (right) for an n-type WS_2 -based photoelectrochemical cell. The electrolyte is 12 M LiBr and $E_{redox} = +0.64$ V vs. SCE; for current density multiply current shown times 32 cm^{-2} , ref. 15.

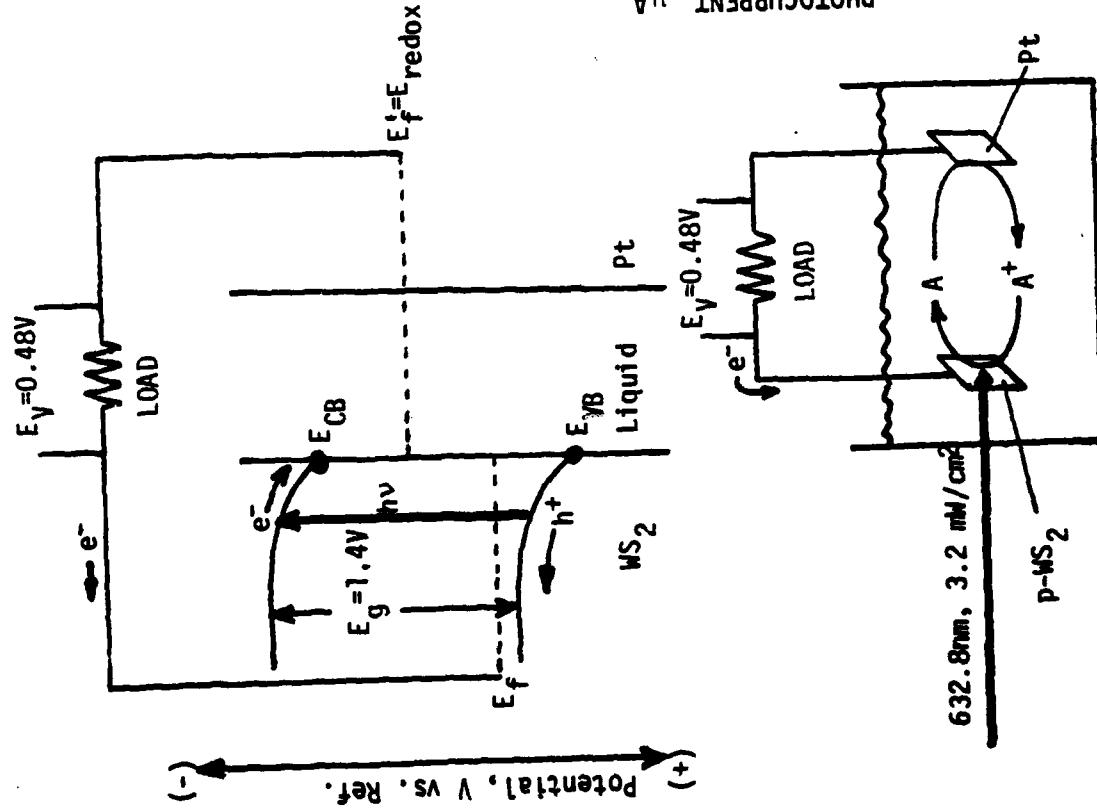
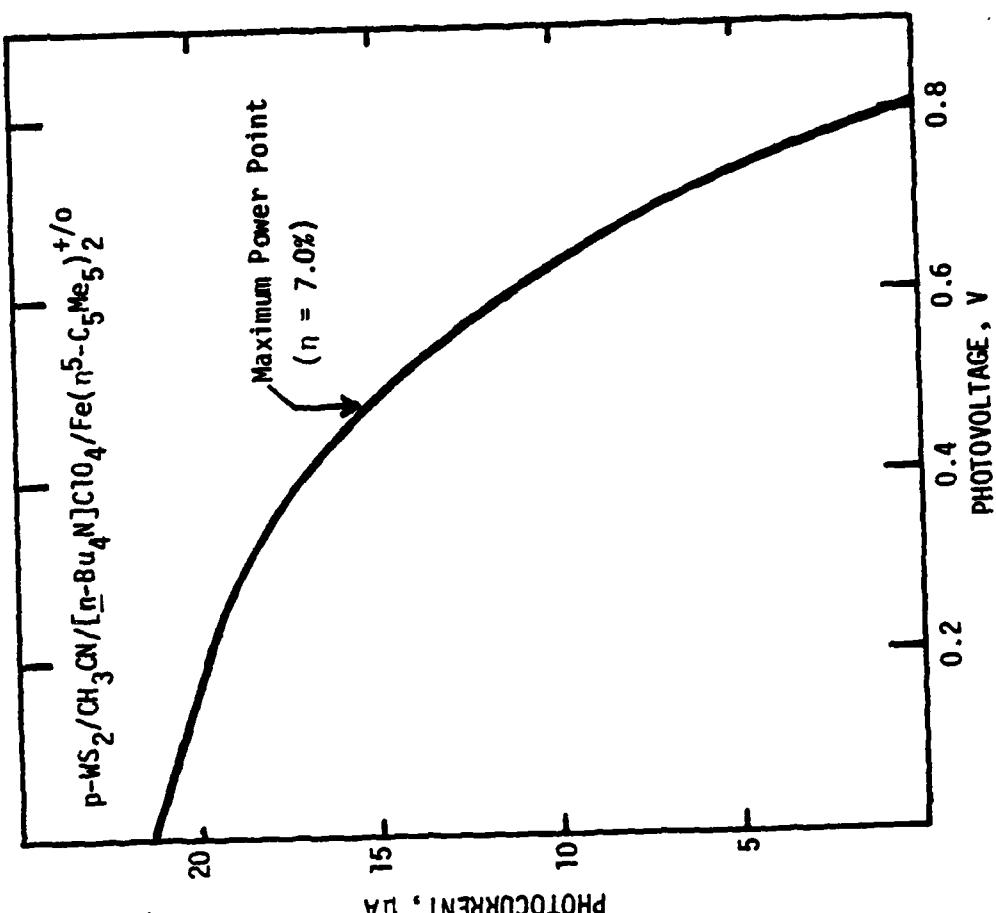
Figure 2. Cell (lower left), cell energetics at maximum power point (upper left) and output characteristics (right) for a p-type WS_2 -based photoelectrochemical cell. The E_{redox} is -0.38 V vs. Ag^+/Ag ; for current density multiply current shown by 32 cm^{-2} , ref. 16.

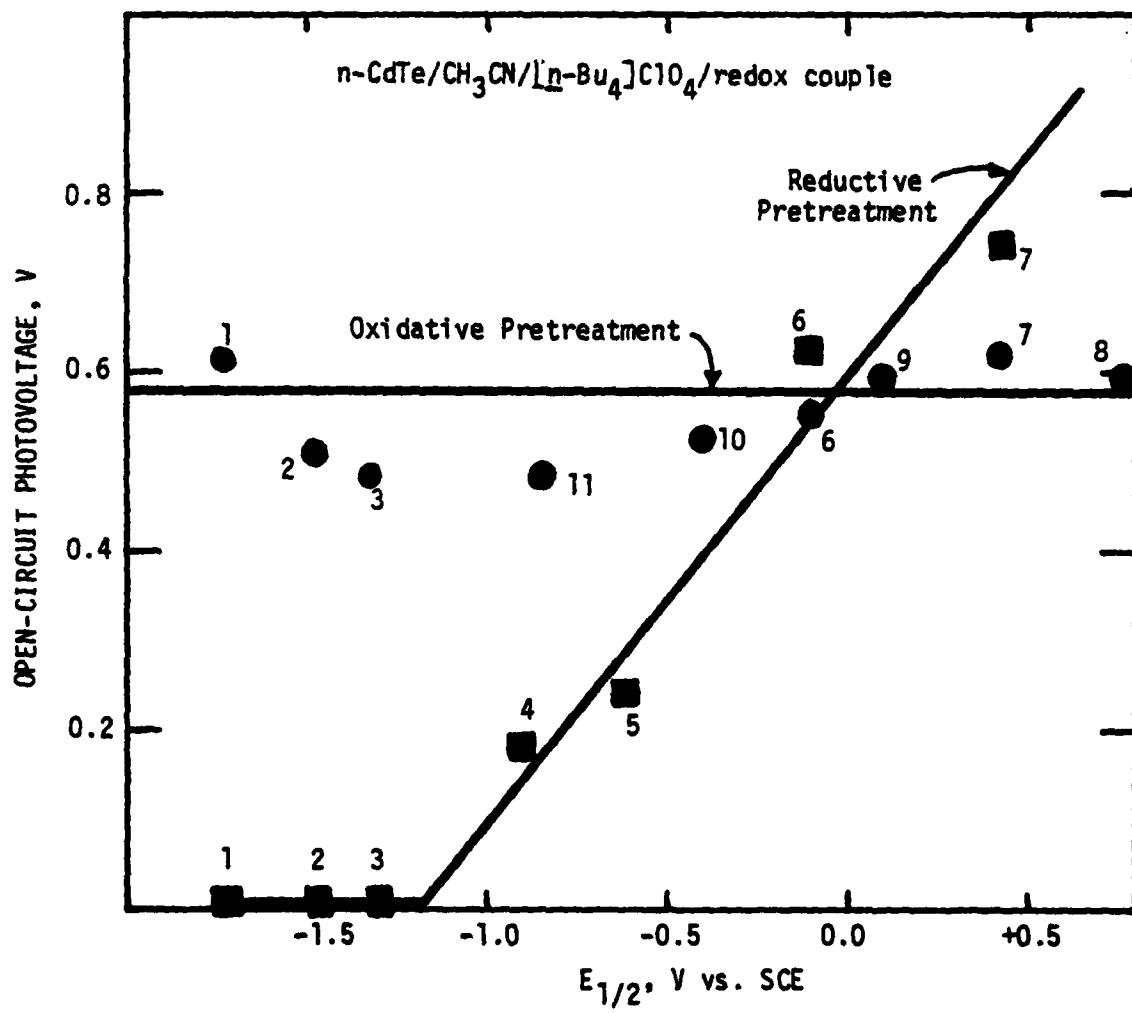
Figure 3. Photovoltage from n-CdTe etched with an oxidizing etch (●) or an oxidizing etch followed by a reducing treatment ($NaOH/S_2O_4^{2-}$) (■) is a function of $E_{1/2}$ of a contacting couple. The numbers refer to redox couples: 1- $Ru(bipy)_3^{0/-}$; 2- $Ru(bipy)_3^{+/0}$; 3- $Ru(bipy)_3^{2+/+}$; 4- $TQ^{+/0}$; 5- $TQ^{2+/+}$; 6- $Fe(n^5-C_5Me_5)_2^{+/0}$; 7- $Fe(n^5-C_5H_5)_2^{+/0}$; 8- $TMPD^{2+/+}$; 9- $TMPD^{+/0}$; 10- $MV^{2+/+}$; 11- $MV^{+/0}$; see ref. 18.

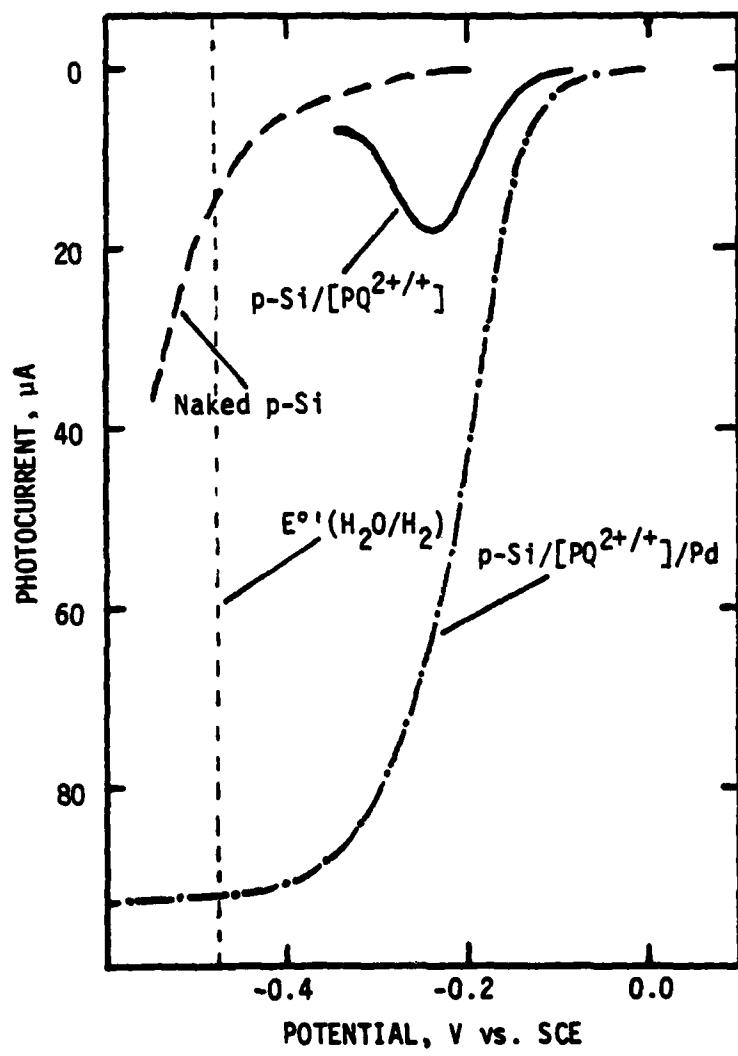
Figure 4. Comparison of photocathodic current (632.8 nm; $\sim 6 \text{ mW/cm}^2$) for naked p-type Si (----), p-type Si bearing $[(PQ^{2+})_n]_{surf.}$, p-type Si bearing $[(PQ^{2+})_n]_{surf.}$ (—), and p-type Si bearing $[(PQ^{2+})_n]_{surf.}/Pd(O)$ (---) at pH = 4. The photocathodic current in the latter case is associated with H_2 evolution that occurs more positive than $E^0(H_2O/H_2)$. For current density multiply values shown by 10 cm^{-2} . The current peak for the smooth curve is associated with the uphill reduction $[(PQ^{2+})_n]_{surf.} \rightarrow [(PQ^+)_n]_{surf.}$, see ref. 49.

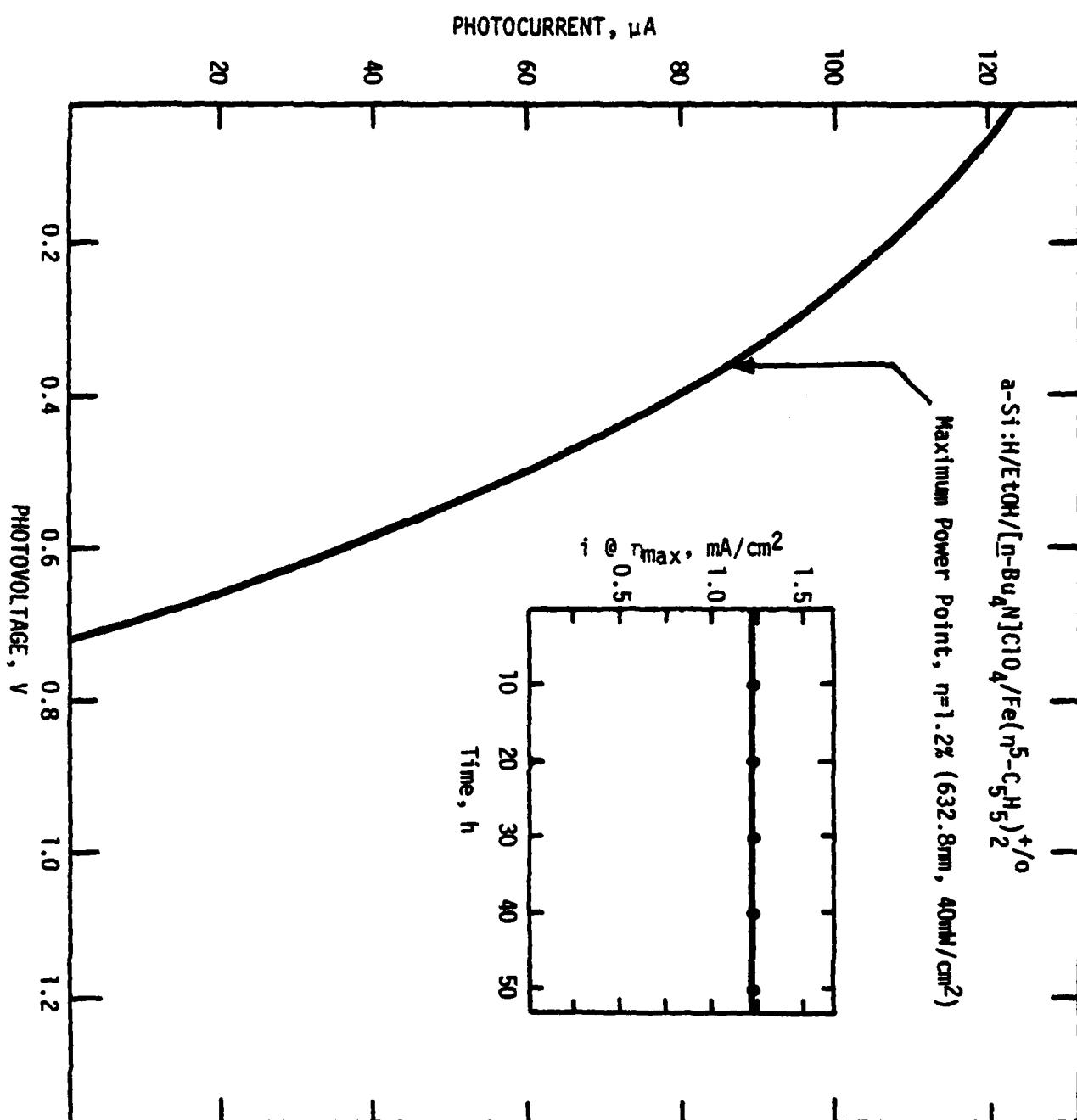
Figure 5. Output characteristics and photocurrent density at maximum power point against time (inset) for an intrinsic a-Si:H photoanode based cell, see ref. 5.











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